RESEARCH REPORT

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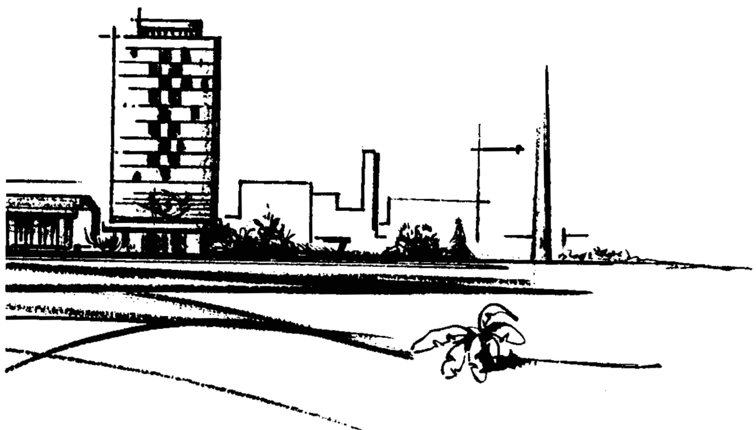

GPO PRICE $ ______

CSFTI PRICE(S) $ ______

Hard copy (HC) $1.00

Microfiche (MF) .50

ff 653 July 65

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TWENTY-SECOND QUARTERLY PROGRESS REPORT

on

INVESTIGATION OF MECHANICAL PROPERTIES OF CHROMIUM, CHROMIUM-RHENIUM, AND DERIVED ALLOYS

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

September 15, 1965

by

A. Gilbert

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September 15, 1965

National Aeronautics and Space
Administration
Office of Research Grants and Contracts
Office of Space Sciences
600 Independence Boulevard
Washington, D.C. 20546

Attention Mr. T.L.K. Smull, Code RU

Gentlemen:

"Investigation of Mechanical Properties of Chromium,
Chromium-Rhenium, and Derived Alloys",
Contract No. NASW-101, HS-180

This letter accompanies 25 copies of the Twenty-Second Quarterly Progress Report describing work on the above contract during the period July 1 to September 30, 1965.

Very truly yours,

A. Gilbert

A. Gilbert
Metal Science Group

AG:tam
Enc. (25)

cc: Mr. J. Maltz (2)
Mr. W. D. Klopp

INVESTIGATION OF MECHANICAL PROPERTIES OF CHROMIUM, CHROMIUM-RHENIUM, AND DERIVED ALLOYS

by

A. Gilbert

QUENCHED-IN DEFECTS IN Mo-35Re

INTRODUCTION

Experiments performed in an earlier phase of this program showed that a major effect of high rhenium additions to molybdenum was to modify the preferred slip plane.(1) In brief, whereas molybdenum slips exclusively on {110} planes, both {112} and {123} slip planes were observed in Mo-35Re. In order to shed further light on the mechanism underlying this modification of the slip plane, some approach is necessary which is sensitive to the way in which rhenium affects various physical properties of the lattice. It was considered that such information could be derived from a study of the factors affecting the formation and stability of quenched-in vacancy clusters in molybdenum and molybdenum-rhenium alloys, since previous experiments performed on a wide range of face-centered cubic (fcc) metals and alloys quenched from close to the melting point have been a rich source of information on the fundamental properties of the fcc lattice. Examples of such information are as follows:

1. <u>The relationship between the type of vacancy clusters and the stacking-fault energy of the metal.</u>

It has been found experimentally that several types of lattice defects may be produced in quenched and aged metals and alloys supersaturated with vacancies. Materials of low stacking-fault energies frequently produce three-dimensional tetrahedra consisting of stacking faults on the {111} planes such as those seen in Au[2] and Ni-Co alloys. Aluminum and aluminum alloys, on the other hand, with a higher stacking-fault energy, produce two-dimensional loops[3] of various kinds. By controlled aging studies allied to electron microscope observations, it is possible to make estimates of stacking-fault energies for alloys exhibiting either type of defect.

2. <u>The crystal plane on which vacancy loops condense, and their Burgers vector.</u>

In fcc materials, loops condense on {111} planes with an $\frac{a}{2}\langle 110\rangle$ or an $\frac{a}{3}\langle 111\rangle$ Burgers vectors. In irradiated body centered cubic (bcc) materials, however, loops with Burgers vectors of $\frac{a}{2}\langle 111\rangle$ and also a $\langle 100\rangle$ have been observed on {110} planes.[4] In both fcc and bcc materials, a particular configuration is chosen so as to minimize the energy of the defect. Such observations can thus point to the parameters which are the most important in determining this energy.

3. <u>The binding energy of a vacancy to a solute atom.</u>

A type of defect known as a helical dislocation can be formed when dislocations in the screw orientation absorb vacancies. Such helices are found to be most stable in alloys, and the stability of this type of defect is thought to be a function of the binding energy between a vacancy and a solute atom.[5]

In bcc metals, however, until very recently there was no evidence from either annealing studies or transmission microscopy that high vacancy supersaturations could be quenched-in. Part of the reason for this may be that, in general, bcc materials have much higher melting points than fcc. This makes it difficult to achieve a sufficiently high quenching rate to produce the necessary supersaturation of vacancies, since the amount of heat which must be rapidly dissipated from the quenched sample increases with the annealing temperature. Even in nickel, a fcc metal with a moderately high melting point (1453°C), there is as yet no good evidence that vacancy clusters have successfully been quenched-in.

Another contributing factor, as pointed out by Gregory[6], may be that, while for fcc materials the energy of vacancy formation E_f and of movement E_m are roughly in the ratio 3:2, the ratio E_f:E_m for bcc metals is estimated to be closer to 4:1. Thus, vacancies are relatively much more mobile at a given temperature in bcc materials than in fcc and quenching experiments correspondingly more difficult. In addition, because of the relatively high formation energy, the original equilibrium vacancy concentration at the annealing temperature may be much lower than for the fcc metals.[†]

Finally, if the concentration of vacancies is intrinsically low in bcc materials, it may well be that the commonly observed interstitial impurity levels of 10 to 1000 ppm can tie up and effectively prevent clustering of the thermal vacancies generated.

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† The thermal vacancy concentration, c, at temperature, T, is given by $c = e^{-E_f/kT}$.

Despite these difficulties, however, Lawley, Meakin, and Koo[7] have successfully quenched pure molybdenum single crystals from 2600°C to produce a high supersaturation of vacancies at room temperature, which on annealing at 400°C agglomerated to produce loops.

The relevance of the preceding discussion to the present program is that one of the original hypotheses advanced to explain the beneficial effect of rhenium additions to the ductility of the Group VI-A transition metals was the effect of rhenium in changing the stacking-fault energy. Now that it is known that vacancy defects can be quenched into molybdenum, the development of a technique for quenching vacancies into Mo-35Re would perhaps permit a comparison to be made between the stacking-fault energy of molybdenum and that of Mo-35Re. Furthermore, it has been observed in another phase of the Integrated Chromium Alloy Program that precipitation kinetics in Cr-35Re are very much slower than in pure chromium.[8] Comparative quenching experiments in molybdenum and Mo-35Re should show whether or not there is a preferential binding between the substitutional solute, rhenium, and vacancies which could explain this kinetic effect. Finally, it has been observed that Mo-35Re prefers different slip planes to those of unalloyed molybdenum. In this context, it would be interesting to know whether vacancy loops also prefer to condense on different planes in molybdenum and Mo-35Re. Thus, a study of vacancy-annealing processes by transmission electron microscopy could be a powerful tool in explaining the mechanism underlying several effects already experimentally verified in earlier phases of this program. The present report describes a preliminary attempt to examine the feasibility of developing the appropriate techniques.

EXPERIMENTAL PROCEDURES

Because of the known difficulties involved in quenching bcc materials, it is desirable to start with as few vacancy sinks (random dislocations, dislocation networks, or grain boundaries) as possible and also, in order to minimize immobilizing interactions between interstitials and vacancies, to use as pure starting material as possible. In addition, in order to attain a sufficiently high cooling rate, quenching specimens should be in the form of sheet.

Accordingly, sheet samples were prepared by cross rolling 1/2-inch lengths of 1/8-inch-diameter Mo-35Re rod donated by the Chase Brass and Copper Company. Sheet thicknesses in the range 10 to 20 mils were employed. After rolling, samples were annealed for periods of 2 to 8 hours in a hydrogen atmosphere at temperatures in the range 2100 to 2300°C, in order to produce some degree of purification. Sheet quenching samples, approximately 1 inch long by 1/2 inch wide, were then slowly heated up in a tantalum-element furnace to temperatures in the range 2400 to 2500°C, keeping the vacuum better than 2×10^{-4} mms of mercury. Specimens were annealed at the maximum temperature for periods from 5 to 20 minutes, and then were quenched into liquid tin. The specimens were dropped either mechanically or by suspending the quenching sample and a small tungsten weight by a 5- to 10-mil wire of Mo-35Re, which crept to failure at a temperature close to its melting point.

After retrieval from the molten tin, the sheet samples were cleaned (from remaining tin) in hydrochloric acid, and thin foils were prepared for transmission microscopy by electrolytic dissolution in alcohol and sulfuric acid. The foils were mounted in a tilting holder and examined in a Siemens Elmiskop 1A.

EXPERIMENTAL RESULTS

The grain sizes produced by the annealing treatment prior to the quench were generally very fine (of the order of 0.2-mm grain diameter), reflecting the great difficulty of grain growth even at temperatures close to the melting point. In addition, depending on the exact history of a particular specimen, there were many instances of dislocation networks inhomogeneously distributed within the grains, and also on occasions a fairly high density of random dislocations. This, unfortunately, provides a large number of grain-boundary sinks to which vacancies can diffuse during the quench. Nonetheless, in spite of these fairly severe restrictions on what might be expected, evidence was obtained that vacancies had been quenched-in. This evidence was in the form of helical dislocations, examples of which are presented in Figures 1 and 2.

Figure 1(a) shows an example of a stable helix at the left-hand side of the figure, and parallel to it, several rows of dislocation loops which were probably produced by degeneration of helices. A twin is visible at the right-hand side of the figure. Figure 1(b) shows examples of loops and helices in another area of the same foil. Figure 2(a) shows an area containing short left-handed and right-handed helices similar to those observed in aluminum by Westmacott, et al.[9], and Figure 2(b) shows rows of aligned loops.

In different areas of one grain in this particular foil, helices were observed with axes lying along three different {111} directions. This is consistent with dislocations having a {111} type Burgers vector since helices are formed by the absorption of vacancies by screw dislocations, and the Burgers vector of a screw dislocation is parallel to its length. No direct determination of Burgers vector has yet been made. However, one series of photographs and associated diffraction patterns showed out-of-contrast loops under 2-beam conditions consistent with an {001} or {111} type Burgers vector, but not a {110} type Burgers vector.

The loops visible in Figure 1 lie on {110} planes. The projected loops in Figure 2 however are sufficiently close to being circular that it is difficult to determine the major and minor axes. One {112} and two {110} type planes satisfy the geometrical considerations within experimental error.

DISCUSSION

The loops and helices shown in Figures 1 and 2 are thought to be the first examples of such defects observed in quenched bcc materials. The observation of helices rather than loops (as observed in unalloyed molybdenum) may be a result of a different quenching temperature as an alloy effect. It has been observed in fcc materials that helical dislocations are formed where the annealing temperature has been too low to produce a sufficiently high vacancy supersaturation for a more homogeneous loop nucleation to occur.[10] Alternatively, helices are also formed in alloys having a high binding energy between a vacancy and a solute atom.[5] Until a more complete investigation into the effect of quenching temperatures on quenched-in defects has been made, it will not be possible to distinguish between the two possibilities.

The purpose of the preliminary experiments described in this report was primarily to investigate the feasibility of using this type of quenching experiment to study the effect of rhenium on vacancy clustering in molybdenum. This has clearly been established. Experiments planned for the future will investigate the effect of pre-quench annealing temperatures and post-quench aging temperatures on the type of defect observed.

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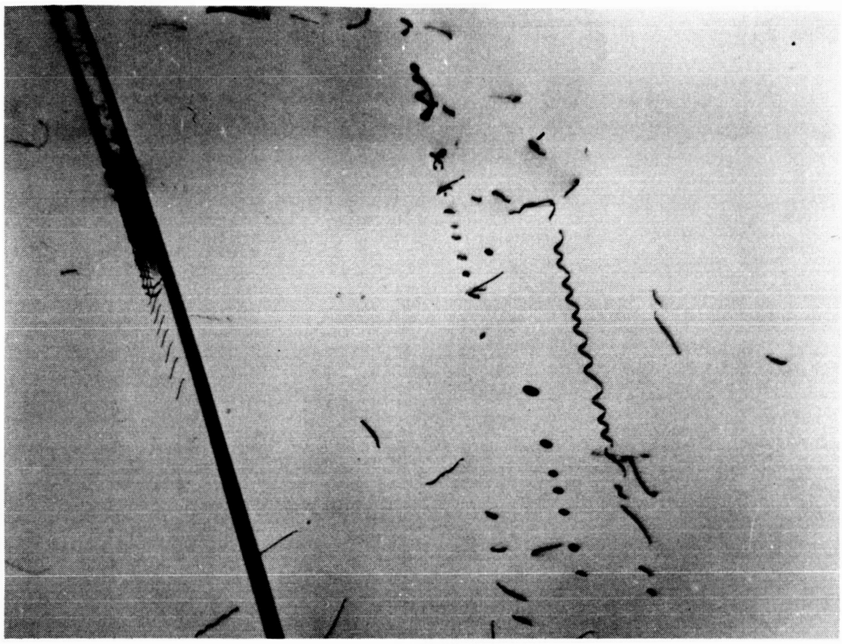
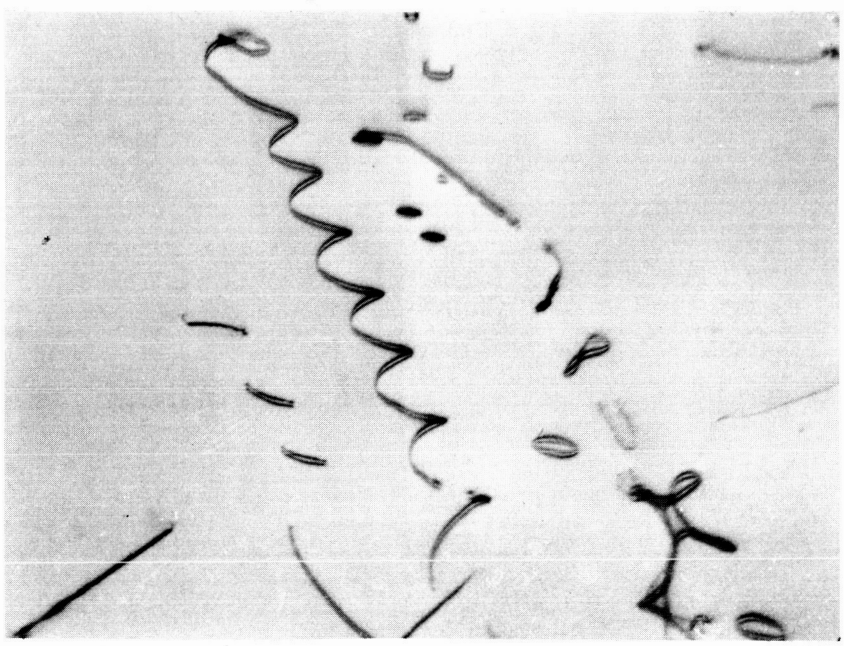
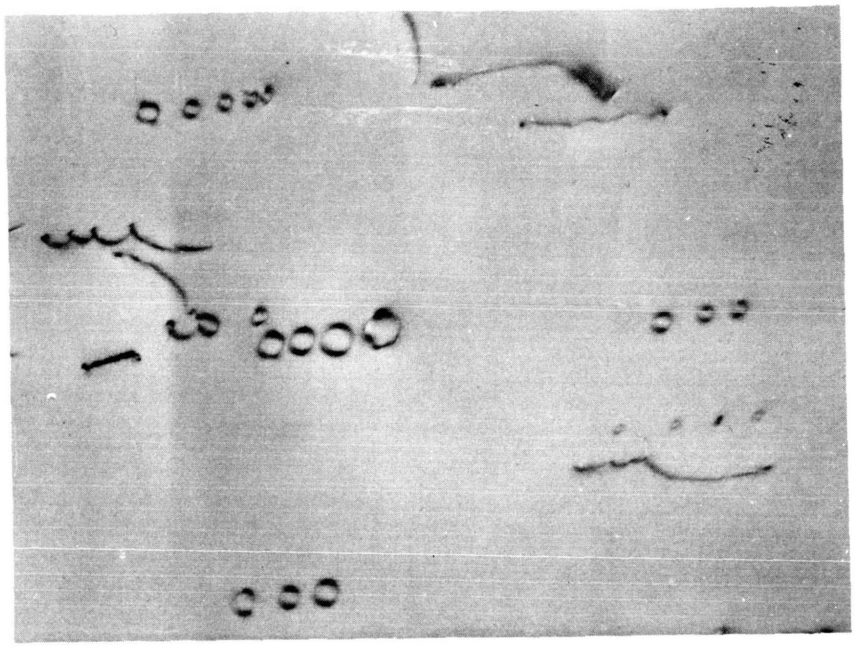


a. (15,000X)

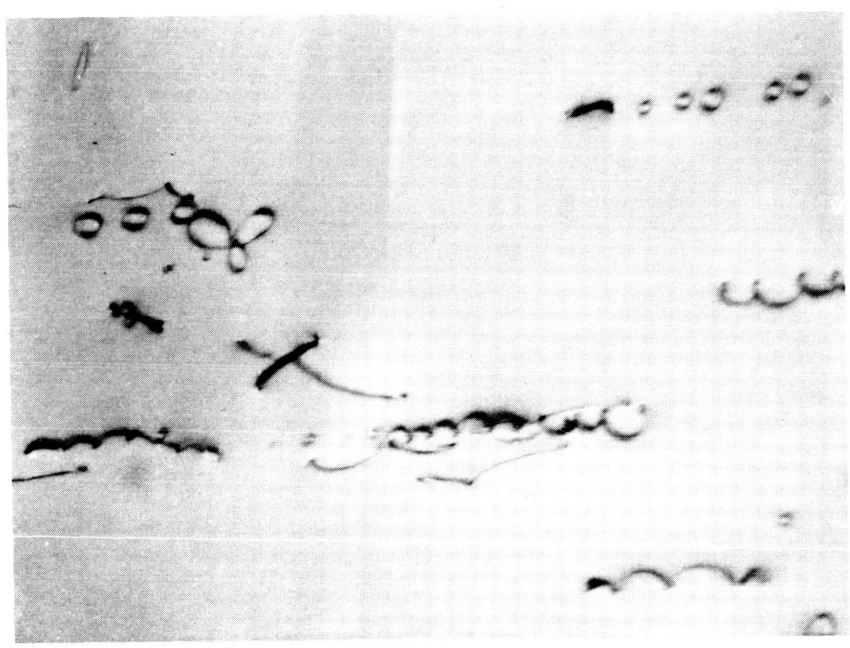


b. (30,000X)

FIGURE 1. HELICAL DISLOCATIONS AND DISLOCATION LOOPS IN QUENCHED AND AGED Mo-35Re



a. (30,000X)



b. (30,000X)

FIGURE 2. HELICAL DISLOCATIONS AND DISLOCATION LOOPS IN QUENCHED AND AGED Mo-35Re

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